

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
30 January 2003 (30.01.2003)

PCT

(10) International Publication Number
WO 03/008417 A1(51) International Patent Classification⁷: C07D 487/04,
A01N 43/90 // (C07D 487/04, 249:00, 239:00)

(21) International Application Number: PCT/EP02/07578

(22) International Filing Date: 8 July 2002 (08.07.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
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AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

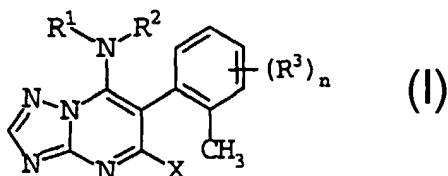
(48) Date of publication of this corrected version:

30 October 2003

(15) Information about Correction:

see PCT Gazette No. 44/2003 of 30 October 2003, Sec-
tion IIFor two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: SUBSTITUTED 6-(2-TOLYL)-TRIAZOLOPYRIMIDINES AS FUNGICIDES



with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted; R³ is halogen, cyano, alkyl, alkoxy, haloalkyl, or C(=O)A, wherein A is hydrogen, hydroxy, alkyl, amino, or mono- or dialkyl-amino; n is an integer from 1 to 4; and X is halogen, cyano, alkyl, alkoxy, haloalkoxy or alkenyloxy; processes for their preparation, compositions containing them and to their use for combating phytopathogenic fungi.

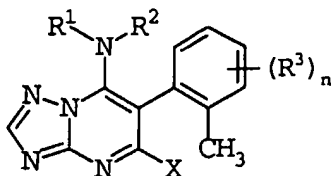
SUBSTITUTED 6-(2-TOLYL)-TRIAZOLOPYRIMIDINES AS FUNGICIDES

Description

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The invention relates to substituted 6-(2-tolyl)-triazolopyrimidines of formula I

10



I

in which

15

R¹ and R² independently denote hydrogen or C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, or C₄-C₁₀-alkadienyl, C₁-C₁₀-haloalkyl, C₂-C₁₀-haloalkenyl, C₃-C₁₀-cycloalkyl, phenyl, naphthyl, or

20

5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

25

where R¹ and R² radicals may be unsubstituted or partly or fully halogenated or may carry one to three groups R^a,

30

R^a is cyano, nitro, hydroxyl, C₁-C₆-alkyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-C₁-C₆-alkylamino, C₂-C₆-alkenyl, C₂-C₆-alkenyloxy, C₂-C₆-alkynyl, C₃-C₆-alkynyloxy and C₁-C₄-alkylenedioxy; or

35

R¹ and R² together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted by one to three R^a radicals;

40

R³ is halogen, cyano, C₁-C₁₀-alkyl, C₁-C₁₀-alkoxy, C₁-C₁₀-haloalkyl, or C(=O)A, wherein

45

A is hydrogen, hydroxy, C₁-C₈-alkyl, C₁-C₈-alkoxy, amino, C₁-C₈-alkylamino, or di-(C₁-C₈-alkyl)-amino;

2

n is an integer from 1 to 4; and

X is halogen, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₈-alkenyloxy.

5

Moreover, the invention relates to processes for their preparation, compositions containing them and to their use for combating phytopathogenic fungi.

10 6-Phenyl-7-amino-triazolopyrimidines are generally known from US 4,567,262 and US 5,593,996.

Triazolopyrimidines with a trifluorophenyl group in 6-position are disclosed in WO-A 98/46607 and EP-A 945 453.

15

From WO-A 98/46608 diverse 6-phenyl-triazolopyrimidines are known, which are substituted in the 7-position by fluorinated alkylamines.

20 The compounds disclosed in the documents discussed above are said to be active against various phytopathogenic fungi.

It is an object of the present invention to provide compounds having improved fungicidal activity.

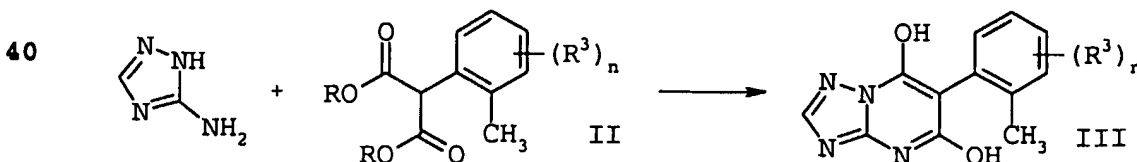
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We have found that this object is achieved by the compounds defined at the outset. Furthermore, we have found processes for their preparation, compositions comprising them and methods for controlling phytopathogenic fungi using the compounds I.

30

The compounds of the formula I differ from the compounds known from closest prior art WO-A 98/46608 in the 2-tolyl group, which is further substituted.

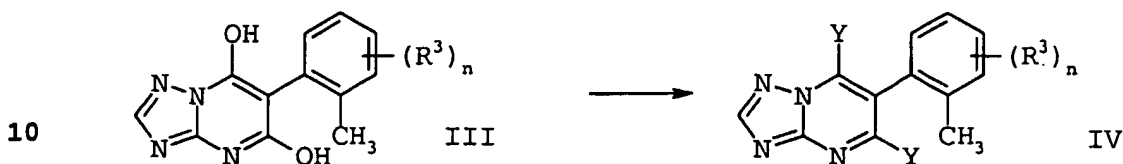
35 The present invention further provides a process for the preparation of compounds of formula I as defined above which comprises reacting 5-amino-triazole with 2-(2-tolyl)-substituted malonic acid ester of formula II, in which



R represents alkyl, preferably C₁-C₆-alkyl, in particular methyl or ethyl, under alkaline conditions, preferably using high boiling tertiary amines as for example tri-n-butylamine as disclosed for example by EP-A 770 615 to yield compounds of formula III.

3

The resulting 5,7-dihydroxy-6-phenyl-triazolopyrimidine of formula III, wherein R^3 and n are as defined for formula I, is subsequently treated with a halogenating agent, preferably with a brominating or chlorinating agent, such as phosphorus oxybromide or phosphorus oxychloride, neat or in the presence of a solvent to give IV.



The reaction is suitably carried out at a temperature in the range from 0 °C to 150 °C, the preferred reaction temperature being from 80 °C to 125 °C as disclosed for example by EP-A 770 615.

Dihalo-triazolopyrimidine IV is further reacted with an amine of formula V

20



in which R^1 and R^2 are as defined in formula I to produce compounds of formula I in which X is halogen.

25

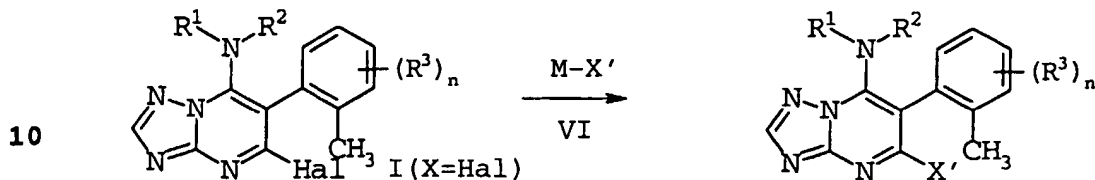
The reaction between the 5,7-dihalo compound IV and the amine of formula V can be carried out under conditions known from WO-A 98/46608. The reaction is preferably carried out in the presence of a solvent. Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons such as dichloromethane and aromatic hydrocarbons, for example toluene.

The reaction is suitably carried out at a temperature in the range from 0°C to 70°C, the preferred reaction temperature being from 10°C to 35°C.

It is also preferred that the reaction is carried out in the presence of a base. Suitable bases include tertiary amines, such as triethylamine, and inorganic bases, such as potassium carbonate or sodium carbonate. Alternatively, an excess of the compound of formula V may serve as a base.

Compounds of formula I in which X denotes cyano, C_1 - C_6 -alkoxy, C_1 - C_6 -haloalkoxy or C_3 - C_8 -alkenyloxy can be prepared by reacting compounds I in which X is halogen, preferably chloro, with compounds of formula VI, which are, dependent from the value of X'

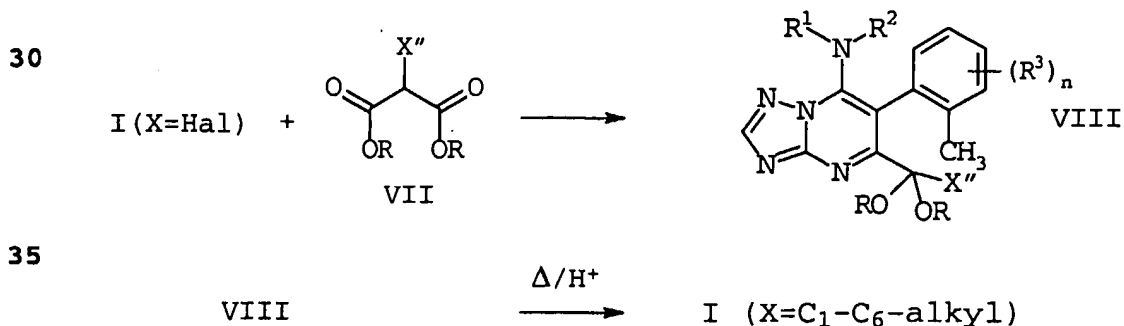
to be introduced to yield formula I compounds, an anorganic cyano salt, an alkoxylate, haloalkoxylate or an alkenyloxylate, respectively, preferably in the presence of a solvent. The cation M in formula VI has minor influence; for practical and economical reasons usually ammonium-, tetraalkylammonium- or alkalimetal- and earth metal salts are preferred.



The reaction is suitably carried out at a temperature in the range from 0 to 120°C, the preferred reaction temperature being from 10 to 40°C [cf. J. Heterocycl. Chem., Vol.12, p. 861-863 (1975)].

Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons such as dichloromethane and aromatic hydrocarbons, for example toluene.

Compounds of formula I in which X denotes C₁-C₆-alkyl can be prepared by reacting compounds I in which X is halogen, preferably chloro, with malonic acid esters of formula VII, wherein X" denotes H or C₁-C₅-alkyl and R denotes C₁-C₄-alkyl, to compounds of formula VIII and decarboxylation under conditions described in US 5,994,360.



Accordingly, the invention relates to the novel intermediates of formulae II, III and IV.

The compounds of formula II are preferably prepared by reaction of the corresponding substituted bromobenzenes with sodium dialkylmalonates in the presence of a copper(I) salt [cf. Chemistry Letters, pp. 367-370, 1981; EP-A 10 02 788].

5

The compounds of formula II may also be prepared by reaction of an alkyl 2-(2-tolyl)-acetate with dialkylcarbonate in the presence of a strong base, preferably sodium ethoxide and sodium hydride (cf. Heterocycles, pp. 1031-1047, 1996).

5

The substituted phenylacetates which are the starting compounds for compounds of formula II are known and commercially available, and/or they are obtainable by generally known methods.

- 10 The reaction mixtures are worked up in a customary manner, for example by mixing with water, phase separation and, if required, chromatographic purification of the crude products. Some of the end products are obtained in the form of colorless or slightly brownish, viscous oils, which are purified or freed from volatile
- 15 components under reduced pressure and at moderately elevated temperatures. If the end products are obtained as solids, purification can also be carried out by recrystallization or digestion.

- If individual compounds I are not obtainable by the routes described above, they can be prepared by derivatization of other compounds I.
- 20

- In the symbol definitions given in the formulae above, collective terms were used which generally represent the following substituents:
- 25

- halogen: fluorine, chlorine, bromine and iodine;
- C₁-C₁₀-alkyl: saturated, straight-chain or branched hydrocarbon radicals having 1 to 10, especially 1 to 6 carbon atoms, for example C₁-C₄-alkyl as mentioned above or pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-di-methylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;
- 40 - C₂-C₁₀-alkenyl: unsaturated, straight-chain or branched hydrocarbon radicals having 2 to 10, especially 2 to 6 carbon atoms and a double bond in any position, for example ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl,
- 45 1-methyl-2-propenyl and 2-methyl-2-propenyl;

6

C₂-C₁₀-alkynyl: straight-chain or branched hydrocarbon radicals having 2 to 10, especially 2 to 4 carbon atoms and a triple bond in any position, for example ethynyl, 1-propynyl, 2-propynyl, 1-butyne, 2-butyne, 3-butyne and 1-methyl-2-propynyl;

- 5
- C₁-C₁₀-haloalkyl and haloalkyl moieties of C₁-C₆-haloalkoxy: straight-chain or branched alkyl groups having 1 to 6 or 10, preferably 1 to 4 carbon atoms (as mentioned above), where the hydrogen atoms in these groups may be partially or fully replaced
- 10 by halogen atoms as mentioned above, for example C₁-C₂-haloalkoxy, such as chloromethoxy, bromomethoxy, dichloromethoxy, trichloromethoxy, fluoromethoxy, difluoromethoxy, trifluoromethoxy, chlorofluoromethoxy, dichlorofluoromethoxy, chlorodifluoromethoxy, 1-chloroethoxy, 1-bromoethoxy,
- 15 1-fluoroethoxy, 2-fluoroethoxy, 2,2-difluoroethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro-2,2-difluoroethoxy, 2,2-dichloro-2-fluoroethoxy, 2,2,2-trichloroethoxy and pentafluoroethoxy;
- 20 C₃-C₁₀-cycloalkyl: mono- or bicyclic cycloalkyl groups having 3 to 10 carbon atoms; monocyclic groups preferably have 3 to 8, especially 3 to 6 ring members, bicyclic groups preferably have 8 to 10 ring members.
- 25 A 5- or 6-membered heterocyclyl group, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, preferably one oxygen atom, for example 1-pyrimidinyl, 2-pyrimidinyl, morpholin-4-yl.
- 30 5-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom: 5-membered heteroaryl groups which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members, for example
- 35 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 1,2,4-oxa-
- 40 diazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 1,2,4-triazol-3-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl and 1,3,4-triazol-2-yl;
- 6-membered heteroaryl, containing one to four nitrogen atoms:
- 45 6-membered heteroaryl groups which, in addition to carbon atoms, may contain one to three or one to four nitrogen atoms as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-py-

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ridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl and 1,2,4-triazin-3-yl.

With respect to their intended use, preference is given to
5 triazolopyrimidines of the formula I having the following substituents, where the preference is valid in each case on its own or in combination:

A preferred cycloalkyl moiety is cyclopentyl being optionally
10 substituted by one or more nitro, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy groups.

A preferred heteroaryl moiety is pyridyl, pyrimidyl, pyrazolyl or thienyl.
15

Preference is given to compounds of formula I in which any alkyl or haloalkyl part of the groups R¹ or R², which may be straight chained or branched, contains up to 10 carbon atoms, preferably 1 to 9 carbon atoms, more preferably 2 to 6 carbon atoms, any
20 alkenyl or alkynyl part of the substituents R¹ or R² contains up to 10 carbon atoms, preferably 2 to 9 carbon atoms, more preferably 3 to 6 carbon atoms, any cycloalkyl part of the substituents R¹ or R² contains from 3 to 10 carbon atoms, preferably from 3 to 8 carbon atoms, more preferably from 3 to 6 carbon atoms, and any
25 bicycloalkyl part of the substituents R¹ or R² contains from 5 to 9 carbon atoms, preferably from 7 to 9 carbon atoms. Any alkyl, alkenyl or alkynyl group may be linear or branched.

Likewise, preference is given to compounds of formula I wherein R¹
30 is not hydrogen.

Compounds of formula I are preferred in which R¹ represents a straight-chained or branched C₁-C₁₀-alkyl, in particular a branched C₃-C₁₀-alkyl group, a C₃-C₈-cycloalkyl, a C₅-C₉-bicycloalkyl,
35 a C₃-C₈-cycloalkyl-C₁-C₆-alkyl, C₁-C₁₀-alkoxy-C₁-C₆-alkyl, a C₁-C₁₀-haloalkyl or a phenyl group being optionally substituted by one to three halogen atoms or C₁-C₁₀-alkyl or C₁-C₁₀-alkoxy groups.

Particular preference is given to compounds I in which R² represents hydrogen, C₁-C₁₀-alkyl or C₁-C₁₀-haloalkyl, in particular hydrogen.
40

Besides, particular preference is given to compounds I in which R² is hydrogen.
45

Moreover, particular preference is given to compounds I in which R^2 is methyl.

Furthermore, particular preference is given to compounds I in
5 which R^2 is ethyl.

If R^1 denotes C_1 - C_{10} -haloalkyl, preferably polyfluorinated alkyl, in particular 2,2,2-trifluoroethyl, 2-(1,1,1-trifluoropropyl) or 2-(1,1,1-trifluorobutyl), R^2 preferably represents hydrogen.

10

If R^1 denotes optionally substituted C_3 - C_8 -cycloalkyl, preferably cyclopentyl or cyclohexyl, R^2 preferably represents hydrogen or C_1 - C_6 -alkyl.

15 Moreover, particular preference is given to compounds I in which R^1 and R^2 together with the interjacent nitrogen atom form an optionally substituted heterocyclic ring, preferably an optionally substituted C_3 - C_7 -heterocyclic ring, in particular pyrrolidine, piperidine, tetrahydropyridine, in particular 1,2,3,6-tetrahydro-
20 pyridine or azepane which is optionally substituted by one or more C_1 - C_{10} -alkyl groups.

Preference is given to compounds of formula I in which any alkyl part of the groups R^1 or R^2 , which may be straight chained or
25 branched, contains 1 to 9 carbon atoms, more preferably 2 to 6 carbon atoms, any alkenyl or alkynyl part of the substituents R^1 or R^2 contains 2 to 9 carbon atoms, more preferably 3 to 6 carbon atoms, any cycloalkyl part of the substituents R^1 or R^2 contains from 3 to 10 carbon atoms, preferably from 3 to 8 carbon atoms,
30 more preferably from 3 to 6 carbon atoms, and any bicycloalkyl part of the substituents R^1 or R^2 contains from 7 to 9 carbon atoms. Any alkyl, alkenyl or alkynyl moiety may be linear or branched.

35 Compounds of formula I are preferred in which R^1 represents a straight-chained or branched C_1 - C_{10} -alkyl, in particular branched C_3 - C_{10} -alkyl, a C_3 - C_8 -cycloalkyl, C_5 - C_9 -bicycloalkyl, C_3 - C_8 -cycloalkyl- C_1 - C_6 -alkyl, C_1 - C_{10} -alkoxy- C_1 - C_6 -alkyl, or phenyl being optionally substituted by one to three C_1 - C_{10} -alkyl or C_1 - C_{10} -alkoxy
40 groups.

Particular preference is given to compounds I in which R^2 represents hydrogen or C_1 - C_{10} -alkyl, in particular hydrogen.

45 Moreover, particular preference is given to compounds I in which R^2 is methyl or ethyl.

9

If R^1 denotes an optionally substituted C_3 - C_8 -cycloalkyl group, preferably cyclopentyl or cyclohexyl, R^2 preferably represents hydrogen or C_1 - C_6 -alkyl.

- 5 Moreover, particular preference is given to compounds I in which R^1 and R^2 together with the interjacent nitrogen atom form an optionally substituted heterocyclic ring, preferably an optionally substituted C_3 - C_7 -heterocyclic ring, in particular a pyrrolidine, piperidine, tetrahydropyridine, in particular 1,2,3,6-tetrahydro-
10 pyridine or azepane ring which is optionally substituted by one or more C_1 - C_{10} -alkyl groups.

Likewise, particular preference is given to compounds I in which R^2 is hydrogen.

- 15 Particular preference is also given to compounds I in which n has the value 2 and R^3 groups are in 4- and 6-position.

Moreover, preference is given to compounds I in which a R^3 group
20 is in para-portion.

Furthermore, particular preference is given to compounds I in which $(R^3)_n$ is 4,6-dimethyl.

- 25 Likewise, particular preference is given to compounds I in which $(R^3)_n$ is 4-(C_1 - C_8 -alkoxy)carbonyl, especially 4-methoxycarbonyl.

Besides, particular preference is given to compounds I in which $(R^3)_n$ is 4-methoxy-6-methyl, or 4-fluoro-6-methyl.

- 30 Particular preference is also given to compounds I in which $(R^3)_n$ is 4-fluoro, 6-fluoro, or 4-chloro.

Besides, particular preference is given to compounds I in which X
35 is chloro or bromo, especially chloro.

Moreover, preference is given to compounds I in which X is cyano or methyl.

- 40 Furthermore, particular preference is given to compounds I in which X is methoxy, ethoxy, n-propoxy, iso-propoxy, allyloxy, or 3-methylallyloxy.

The particularly preferred embodiments of the intermediates with
45 respect to the variables correspond to those of the radicals X, R^1 , R^2 and R^3 of formula I.

10

Included in the scope of the present invention are (R) and (S) isomers of compounds of general formula I having a chiral center and the racemates thereof, and salts, N-oxides and acid addition compounds.

5

With respect to their use, particular preference is given to the compounds I compiled in the tables below. The groups mentioned in the tables for a substituent are furthermore for their part, independently of the combination in which they are mentioned, a

10 particularly preferred embodiment of the respective substituents.

Table 1

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

15

Table 2

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 5-chloro and R^1 and R^2 correspond to one row in Table A

20 Table 3

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 6-chloro and R^1 and R^2 correspond to one row in Table A

Table 4

25 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 3-fluoro and R^1 and R^2 correspond to one row in Table A

Table 5

30 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-fluoro and R^1 and R^2 correspond to one row in Table A

Table 6

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 5-fluoro and R^1 and R^2 correspond to one row in Table A

35

Table 7

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 6-fluoro and R^1 and R^2 correspond to one row in Table A

40 Table 8

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 3-methyl and R^1 and R^2 correspond to one row in Table A

Table 9

45 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-methyl and R^1 and R^2 correspond to one row in Table A

11

Table 10

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 11

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 12

10 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 13

15 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 5-methoxy and R^1 and R^2 correspond to one row in Table A

Table 14

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

20

Table 15

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

25 Table 16

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 17

30 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 18

35 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4,6-dimethyl and R^1 and R^2 correspond to one row in Table A

Table 19

40 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A

Table 20

45 Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

12

Table 21

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 22

Compounds of formula I, in which X is chloro, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table 23

10 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

Table 24

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-chloro and
15 R^1 and R^2 correspond to one row in Table A

Table 25

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-chloro and
20 R^1 and R^2 correspond to one row in Table A

Table 26

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 3-fluoro and
 R^1 and R^2 correspond to one row in Table A

25 Table 27

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-fluoro and
 R^1 and R^2 correspond to one row in Table A

Table 28

30 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-fluoro and
 R^1 and R^2 correspond to one row in Table A

Table 29

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-fluoro and
35 R^1 and R^2 correspond to one row in Table A

Table 30

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 3-methyl and
 R^1 and R^2 correspond to one row in Table A

40

Table 31

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-methyl and
 R^1 and R^2 correspond to one row in Table A

45

13

Table 32

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 33

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 34

- 10 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 35

- 15 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-methoxy and R^1 and R^2 correspond to one row in Table A

Table 36

- 20 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

Table 37

- 25 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

25 Table 38

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 39

- 30 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 40

- 35 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4,6-dimethyl and R^1 and R^2 correspond to one row in Table A

Table 41

- 40 Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A

Table 42

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

14

Table 43

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 44

Compounds of formula I, in which X is bromo, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table 45

10 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

Table 46

15 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-chloro and R^1 and R^2 correspond to one row in Table A

Table 47

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-chloro and R^1 and R^2 correspond to one row in Table A

20

Table 48

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 3-fluoro and R^1 and R^2 correspond to one row in Table A

25 Table 49

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-fluoro and R^1 and R^2 correspond to one row in Table A

Table 50

30 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-fluoro and R^1 and R^2 correspond to one row in Table A

Table 51

35 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-fluoro and R^1 and R^2 correspond to one row in Table A

Table 52

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 3-methyl and R^1 and R^2 correspond to one row in Table A

40

Table 53

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-methyl and R^1 and R^2 correspond to one row in Table A

45

15

Table 54

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 55

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 56

10 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 57

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-methoxy
15 and R^1 and R^2 correspond to one row in Table A

Table 58

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

20

Table 59

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

25 Table 60

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 61

30 Compounds of formula I, in which X is cyano, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 62

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4,6-dimethyl
35 and R^1 and R^2 correspond to one row in Table A

Table 63

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A
40

Table 64

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

45

16

Table 65

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 66

Compounds of formula I, in which X is cyano, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table 67

10 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

Table 68

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-chloro
15 and R^1 and R^2 correspond to one row in Table A

Table 69

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-chloro and R^1 and R^2 correspond to one row in Table A

20

Table 70

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 3-fluoro and R^1 and R^2 correspond to one row in Table A

25 Table 71

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-fluoro and R^1 and R^2 correspond to one row in Table A

Table 72

30 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-fluoro and R^1 and R^2 correspond to one row in Table A

Table 73

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-fluoro
35 and R^1 and R^2 correspond to one row in Table A

Table 74

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 3-methyl and R^1 and R^2 correspond to one row in Table A

40

Table 75

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-methyl and R^1 and R^2 correspond to one row in Table A

45

17

Table 76

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 77

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 78

10 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 79

15 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-methoxy and R^1 and R^2 correspond to one row in Table A

Table 80

20 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A

Table 81

25 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 82

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 83

30 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 84

35 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4,6-dimethyl and R^1 and R^2 correspond to one row in Table A

Table 85

40 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A

Table 86

45 Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A

18

Table 87

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 88

Compounds of formula I, in which X is methoxy, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table 89

10 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-chloro and R^1 and R^2 correspond to one row in Table A

Table 90

15 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-chloro and R^1 and R^2 correspond to one row in Table A

Table 91

20 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-chloro and R^1 and R^2 correspond to one row in Table A

Table 92

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 3-fluoro and R^1 and R^2 correspond to one row in Table A

25 Table 93

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-fluoro and R^1 and R^2 correspond to one row in Table A

Table 94

30 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-fluoro and R^1 and R^2 correspond to one row in Table A

Table 95

35 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-fluoro and R^1 and R^2 correspond to one row in Table A

Table 96

40 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 3-methyl and R^1 and R^2 correspond to one row in Table A

Table 97

45 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-methyl and R^1 and R^2 correspond to one row in Table A

19

Table 98

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-methyl and R^1 and R^2 correspond to one row in Table A

5 Table 99

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-methyl and R^1 and R^2 correspond to one row in Table A

Table 100

- 10 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-methoxy and R^1 and R^2 correspond to one row in Table A

Table 101

- 15 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-methoxy and R^1 and R^2 correspond to one row in Table A

Table 102

- Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-methoxy and R^1 and R^2 correspond to one row in Table A
- 20

Table 103

- Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-trifluoromethyl and R^1 and R^2 correspond to one row in Table A
- 25 Table 104
- Compounds of formula I, in which X is methyl, $(R^3)_n$ is 5-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 105

- 30 Compounds of formula I, in which X is methyl, $(R^3)_n$ is 6-trifluoromethyl and R^1 and R^2 correspond to one row in Table A

Table 106

- Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4,6-dimethyl and R^1 and R^2 correspond to one row in Table A
- 35

Table 107

- Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-methoxy-6-methyl and R^1 and R^2 correspond to one row in Table A
- 40

Table 108

- Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-fluoro-6-methyl and R^1 and R^2 correspond to one row in Table A
- 45

Table 109

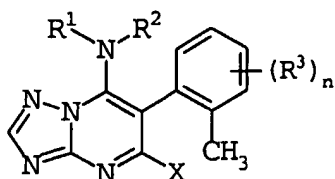
Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-methoxycarbonyl and R^1 and R^2 correspond to one row in Table A

5 Table 110

Compounds of formula I, in which X is methyl, $(R^3)_n$ is 4-cyano and R^1 and R^2 correspond to one row in Table A

Table A

10



I

15

No.	R^1	R^2
A-1	H	H
A-2	CH_2CH_3	H
20 A-3	CH_2CH_3	CH_3
A-4	CH_2CH_3	CH_2CH_3
A-5	CH_2CF_3	H
A-6	CH_2CF_3	CH_3
25 A-7	CH_2CF_3	CH_2CH_3
A-8	CH_2CCl_3	H
A-9	CH_2CCl_3	CH_3
A-10	CH_2CCl_3	CH_2CH_3
30 A-11	$CH_2CH_2CH_3$	H
A-12	$CH_2CH_2CH_3$	CH_3
A-13	$CH_2CH_2CH_3$	CH_2CH_3
A-14	$CH_2CH_2CH_3$	$CH_2CH_2CH_3$
35 A-15	$CH(CH_3)_2$	H
A-16	$CH(CH_3)_2$	CH_3
A-17	$CH(CH_3)_2$	CH_2CH_3
A-18	$(\pm) CH(CH_3)-CH_2CH_3$	H
A-19	$(\pm) CH(CH_3)-CH_2CH_3$	CH_3
40 A-20	$(\pm) CH(CH_3)-CH_2CH_3$	CH_2CH_3
A-21	$(S) CH(CH_3)-CH_2CH_3$	H
A-22	$(S) CH(CH_3)-CH_2CH_3$	CH_3
A-23	$(S) CH(CH_3)-CH_2CH_3$	CH_2CH_3
45 A-24	$(R) CH(CH_3)-CH_2CH_3$	H
A-25	$(R) CH(CH_3)-CH_2CH_3$	CH_3
A-26	$(R) CH(CH_3)-CH_2CH_3$	CH_2CH_3

No.	R ¹	R ²
5	A-27 (±) CH(CH ₃)-CH(CH ₃) ₂	H
	A-28 (±) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
	A-29 (±) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
	A-30 (S) CH(CH ₃)-CH(CH ₃) ₂	H
	A-31 (S) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
10	A-32 (S) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
	A-33 (R) CH(CH ₃)-CH(CH ₃) ₂	H
	A-34 (R) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
	A-35 (R) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
	A-36 (±) CH(CH ₃)-C(CH ₃) ₃	H
15	A-37 (±) CH(CH ₃)-C(CH ₃) ₃	CH ₃
	A-38 (±) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
	A-39 (S) CH(CH ₃)-C(CH ₃) ₃	H
	A-40 (S) CH(CH ₃)-C(CH ₃) ₃	CH ₃
	A-41 (S) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
20	A-42 (R) CH(CH ₃)-C(CH ₃) ₃	H
	A-43 (R) CH(CH ₃)-C(CH ₃) ₃	CH ₃
	A-44 (R) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
	A-45 (±) CH(CH ₃)-CF ₃	H
	A-46 (±) CH(CH ₃)-CF ₃	CH ₃
25	A-47 (±) CH(CH ₃)-CF ₃	CH ₂ CH ₃
	A-48 (S) CH(CH ₃)-CF ₃	H
	A-49 (S) CH(CH ₃)-CF ₃	CH ₃
	A-50 (S) CH(CH ₃)-CF ₃	CH ₂ CH ₃
	A-51 (R) CH(CH ₃)-CF ₃	H
30	A-52 (R) CH(CH ₃)-CF ₃	CH ₃
	A-53 (R) CH(CH ₃)-CF ₃	CH ₂ CH ₃
	A-54 (±) CH(CH ₃)-CCl ₃	H
	A-55 (±) CH(CH ₃)-CCl ₃	CH ₃
	A-56 (±) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
35	A-57 (S) CH(CH ₃)-CCl ₃	H
	A-58 (S) CH(CH ₃)-CCl ₃	CH ₃
	A-59 (S) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
	A-60 (R) CH(CH ₃)-CCl ₃	H
	A-61 (R) CH(CH ₃)-CCl ₃	CH ₃
40	A-62 (R) CH(CH ₃)-CCl ₃	CH ₂ CH ₃
	A-63 CH ₂ C(CH ₃)=CH ₂	H
	A-64 CH ₂ C(CH ₃)=CH ₂	CH ₃
	A-65 CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃

No.	R ¹	R ²
A-66	cyclopentyl	H
A-67	cyclopentyl	CH ₃
5 A-68	cyclopentyl	CH ₂ CH ₃
A-69	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -	
A-70	CH ₂ CF ₂ CF ₃	H
A-71	CH ₂ CF ₂ CF ₃	CH ₃
A-72	CH ₂ CF ₂ CF ₃	CH ₂ CH ₃
10 A-73	CH ₂ CF ₂ CF ₂ CF ₃	H
A-74	CH ₂ CF ₂ CF ₂ CF ₃	CH ₃
A-75	CH ₂ CF ₂ CF ₂ CF ₃	CH ₂ CH ₃

- 15 The compounds I are suitable as fungicides. They have outstanding activity against a broad spectrum of phytopathogenic fungi, in particular from the classes of the *Ascomycetes*, *Deuteromycetes*, *Phycomycetes* and *Basidiomycetes*. Some of them act systemically, and they can be employed in crop protection as foliar- and soil-
20 acting fungicides.

They are especially important for controlling a large number of fungi on a variety of crop plants such as wheat, rye, barley, oats, rice, maize, grass, bananas, cotton, soya, coffee, sugar
25 cane, grapevines, fruit species, ornamentals and vegetables such as cucumbers, beans, tomatoes, potatoes and cucurbits, and on the seeds of these plants.

Specifically, they are suitable for controlling the following
30 plant diseases:

- *Alternaria* species, *Podosphaera* species, *Sclerotinia* species, *Physalospora* canker on vegetables and fruit,
- *Botrytis cinerea* (gray mold) on strawberries, vegetables, ornamentals and grapevines,
- 35 • *Corynespora cassiicola* on cucumbers,
- *Colletotrichum* species on fruit and vegetables,
- *Diplocarpon rosae* on roses,
- *Elsinoe fawcetti* and *Diaporthe citri* on citrus fruit,
- *Sphaerotheca* species on cucurbits, strawberries and roses,
- 40 • *Cercospora* species on peanuts, sugar beets and aubergines,
- *Erysiphe cichoracearum* on cucurbits,
- *Leveillula taurica* on paprika, tomatoes and aubergines,
- *Mycosphaerella* species on apples and japanese apricot,
- *Phyllactinia kakicola*, *Gloeosporium kaki* on japanese apricot,
- 45 • *Gymnosporangium yamadae*, *Leptothyrium pomi*, *Podosphaera leucotricha* and *Gloeodes pomigena* on apples,
- *Cladosporium carpophilum* on pears and japanese apricot,

23

- *Phomopsis* species on pears,
- *Phytophthora* species on citrus fruit, potatoes, onions, especially *Phytophthora infestans* on potatoes and tomatoes,
- *Blumeria graminis* (powdery mildew) on cereals,
- 5 • *Fusarium*- and *Verticillium* species on various plants,
- *Glomerella cingulata* on tee,
- *Drechslera*- and *Bipolaris* species on cereals and rice,
- *Mycosphaerella* species on bananas and peanuts,
- *Plasmopara viticola* on grapevines,
- 10 • *Personospora* species on onions, spinach and chrysanthemum,
- *Phaeoisariopsis vitis* and *Sphaceloma ampelina* on grapefruits,
- *Pseudocercospora herpotrichoides* on wheat and barley,
- *Pseudoperonospora* species on hop and cucumbers,
- *Puccinia* species and *Typhula* species on cereals and turf,
- 15 • *Pyricularia oryzae* on rice,
- *Rhizoctonia* species on cotton, rice and turf,
- *Stagonospora nodorum* and *Septoria tritici* on wheat,
- *Uncinula necator* on grapevines,
- *Ustilago* species on cereals and sugar cane, and
- 20 • *Venturia* species (scab) on apples and pears.

Moreover, the compounds I are suitable for controlling harmful fungi such as *Paecilomyces variotii* in the protection of materials (e.g. wood, paper, paint dispersions, fibers and tissues) and
25 in the protection of stored products.

The compounds I are applied by treating the fungi, or the plants, seeds, materials or the soil to be protected against fungal infection, with a fungicidally active amount of the active ingredients. Application can be effected both before and after infection of the materials, plants or seeds by the fungi.
30

In general, the fungicidal compositions comprise from 0.1 to 95, preferably 0.5 to 90, % by weight of active ingredient.

35

When used in crop protection, the rates of application are from 0.01 to 2.0 kg of active ingredient per ha, depending on the nature of the effect desired.

40 In the treatment of seed, amounts of active ingredient of from 0.001 to 0.1 g, preferably 0.01 to 0.05 g, are generally required per kilogram of seed.

When used in the protection of materials or stored products, the
45 rate of application of active ingredient depends on the nature of the field of application and on the effect desired. Rates of application conventionally used in the protection of materials are,

for example, from 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of active ingredient per cubic meter of material treated.

The compounds I can be converted into the customary formulations, 5 e.g. solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular purpose; in any case, it should guarantee a fine and uniform distribution of the compound according to the invention.

10 The formulations are prepared in a known manner, e.g. by extending the active ingredient with solvents and/or carriers, if desired using emulsifiers and dispersants, it also being possible to use other organic solvents as auxiliary solvents if water is used as the diluent. Auxiliaries which are suitable are essentially: solvents such as aromatics (e.g. xylene), chlorinated 15 aromatics (e.g. chlorobenzenes), paraffins (e.g. mineral oil fractions), alcohols (e.g. methanol, butanol), ketones (e.g. cyclohexanone), amines (e.g. ethanolamine, dimethylformamide) and water; carriers such as ground natural minerals (e.g. kaolins, 20 clays, talc, chalk) and ground synthetic minerals (e.g. highly-disperse silica, silicates); emulsifiers such as non-ionic and anionic emulsifiers (e.g. polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignin-sulfite waste liquors and methylcellulose.

25 Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutyl-naphthalenesulfonic acid, alkylaryl-sulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates and fatty acids and their alkali metal and alkaline earth metal salts, salts of sulfated fatty alcohol glycol ether, condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol or formaldehyde, polyoxyethylene octylphenyl 35 ether, ethoxylated iso-octylphenol, octylphenol, nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol 40 polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocar-

25

bons, e.g. benzene, toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, chloroform, carbon tetrachloride, cyclohexanol, cyclohexanone, chlorobenzene, isophorone, strongly
5 polar solvents, e.g. dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone and water.

Powders, materials for scattering and dusts can be prepared by mixing or concomitantly grinding the active substances with a solid
10 lid carrier.

Granules, e.g. coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredients to solid carriers. Examples of solid carriers are mineral earths,
15 such as silicas, silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable
20 getable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise of from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active ingredient.
25 gredient. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

The following are exemplary formulations:

30 I. 5 parts by weight of a compound according to the invention are mixed intimately with 95 parts by weight of finely divided kaolin. This gives a dust which comprises 5% by weight of the active ingredient.

35 II. 30 parts by weight of a compound according to the invention are mixed intimately with a mixture of 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been sprayed onto the surface of this silica gel. This gives a formulation of the active ingredient with good
40 adhesion properties (comprises 23% by weight of active ingredient).

III. 10 parts by weight of a compound according to the invention are dissolved in a mixture composed of 90 parts by weight of
45 xylene, 6 parts by weight of the adduct of 8 to 10 mol of ethylene oxide and 1 mol of oleic acid N-monoethanolamide, 2 parts by weight of calcium dodecylbenzenesulfonate and 2

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parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 9% by weight of active ingredient).

- 5 IV. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 60 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 5 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isooctylphenol and 5 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 16% by weight of active ingredient).
- 10
- V. 80 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diisobutyl-naphthalene- α -sulfonate, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill (comprises 80% by weight of active ingredient).
- 15
- 20
- VI. 90 parts by weight of a compound according to the invention are mixed with 10 parts by weight of N-methyl- α -pyrrolidone, which gives a solution which is suitable for use in the form of microdrops (comprises 90% by weight of active ingredient).
- 25
- VII. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isooctylphenol and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil. Pouring the solution into 100,000 parts by weight of water and finely distributing it therein gives an aqueous dispersion which comprises 0.02% by weight of the active ingredient.
- 30
- 35
- VIII. 20 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diisobutyl-naphthalene- α -sulfonate, 17 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 60 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill. Finely distributing the mixture in 20,000 parts by weight of water gives a spray mixture which comprises 0.1% by weight of the active ingredient.
- 40
- 45

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The active ingredients can be used as such, in the form of their formulations or the use forms prepared therefrom, e.g. in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, materials
5 for spreading, or granules, by means of spraying, atomizing, dusting, scattering or pouring. The use forms depend entirely on the intended purposes; in any case, this is intended to guarantee the finest possible distribution of the active ingredients according to the invention.

10

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances as such or dissolved in an oil or solvent, can be
15 homogenized in water by means of wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

20

The active ingredient concentrations in the ready-to-use products can be varied within substantial ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

25 The active ingredients may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active ingredient, or even the active ingredient without additives.

30 Various types of oils, herbicides, fungicides, other pesticides, or bactericides may be added to the active ingredients, if appropriate also only immediately prior to use (tank mix). These agents can be admixed with the agents according to the invention in a weight ratio of 1:10 to 10:1.

35

In the use form as fungicides, the compositions according to the invention can also be present together with other active ingredients, e.g. with herbicides, insecticides, growth regulators, fungicides or else with fertilizers. Mixing the compounds I or
40 the compositions comprising them in the use form as fungicides with other fungicides frequently results in a broader fungicidal spectrum of action.

The following list of fungicides, together with which the compounds according to the invention can be used, is intended to illustrate the possible combinations, but not to impose any limitation:

- sulfur, dithiocarbamates and their derivatives, such as iron(III) dimethyldithiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate, manganese ethylenebisdithiocarbamate, manganese zinc ethylenediaminebisdithiocarbamate, tetramethylthiuram disulfide, ammonia complex of zinc (N,N-ethylenebisdithiocarbamate), ammonia complex of zinc (N,N'-propylenebisdithiocarbamate), zinc (N,N'-propylenebisdithiocarbamate), N,N'-polypropylenebis(thiocarbamoyl)disulfide;
- 5 nitro derivatives, such as dinitro(1-methylheptyl)phenyl crotonate, 2-sec-butyl-4,6-dinitrophenyl 3,3-dimethylacrylate, 2-sec-butyl-4,6-dinitrophenylisopropyl carbonate, diisopropyl 5-nitro-isophthalate;
- heterocyclic substances, such as 2-heptadecyl-2-imidazoline acetate, 2,4-dichloro-6-(o-chloroanilino)-s-triazine, 0,0-diethyl phthalimidophosphonothioate, 5-amino-1-[bis(dimethylamino)phosphinyl]-3-phenyl-1,2,4- triazole, 2,3-dicyano-1,4-dithioanthraquinone, 2-thio-1,3-dithiolo[4,5-b]quinoxaline, methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, 2-methoxycarbonylaminobenzimidazole, 2-(2-furyl)benzimidazole, 2-(4-thiazolyl)benzimidazole, N-(1,1,2,2-tetrachloroethylthio)tetrahydrophthalimide, N-trichloromethylthiotetrahydrophthalimide, N-trichloromethylthiophthalimide, 5-Chloro-2-cyano-4-p-tolyl-imidazole-1-sulfonic acid
- 25 dimethylamide, N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfo-diamide, 5-ethoxy-3-trichloromethyl-1,2,3-thiadiazole, 2-thiocyanatomethylthiobenzothiazole, 1,4-dichloro-2,5-dimethoxybenzene, 4-(2-chlorophenylhydrazono)-3-methyl-5-isoxazolone, pyridine-2-thiol 1-oxide, 8-hydroxyquinoline or its copper salt, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine 4,4-dioxide, 2-methyl-5,6-dihydro-4H-pyran-3-carboxanilide, 2-methylfuran-3-carboxanilide, 2,5-dimethylfuran-3-carboxanilide, 2-Chloro-N-(4'-chloro-biphenyl-2-yl)-nicotinamide, 2,4,5-trimethylfuran-3-carboxanilide, N-cyclohexyl- 2,5-dimethylfuran-3-carboxamide, N-cyclohexyl-N-methoxy-2,5-dimethylfuran-3-carboxamide, 2-methylbenzanilide, 2-iodobenzanilide, N-formyl-N-morpholine-2,2,2-trichloroethyl acetal, piperazine-1,4-diylbis-1-(2,2,2-trichloroethyl)formamide, 1-(3,4-dichloroanilino)-1-formylamino-2,2,2-trichloroethane; 2,6-dimethyl-N-tridecylmorpholine or its salts, 2,6-dimethyl-N-cyclododecylmorpholine or its salts, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-cis-2,6-dimethyl- morpholine, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-piperidine, 1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole, 1-[2-(2,4-dichlorophenyl)-4-n-propyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole,
- 45

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N-(n-propyl)-N-(2,4,6-trichlorophenoxyethyl)-N'-imidazolyl-urea, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanol, (2RS,3RS)-1-[3-(2-chlorophenyl)-2-(4-fluorophenyl)-oxiran-2-ylmethyl]-1H-1,2,4-triazole, α -(2-chlorophenyl)- α -(4-chlorophenyl)-5-pyrimidinemethanol, 5-butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine, bis(p-chlorophenyl)-3-pyridinemethanol, 1,2-bis(3-ethoxycarbonyl-2-thioureido)benzene, 1,2-bis(3-methoxycarbonyl-2-thioureido)benzene,

strobilurines such as azoxystrobin, kresoxim methyl, methyl-E-methoxyimino-[α -(2-phenoxyphenyl)]-acetamide, methyl E-methoxyimino-[α -(2,5-dimethylphenoxy)-o-tolyl]acetamide, picoxystrobin, pyraclostrobin, trifloxystrobin,

anilinopyrimidines such as N-(4,6-dimethylpyrimidin-2-yl)aniline, N-[4-methyl-6-(1-propynyl)pyrimidin-2-yl]-aniline, N-[4-methyl-6-cyclopropylpyrimidin-2-yl]aniline, phenylpyrroles such as 4-(2,2-difluoro-1,3-benzodioxol-4-yl)pyrrole-3-carbonitrile,

cinnamamides such as 3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)acryloylmorpholine, 3-(4-fluorophenyl)-3-(3,4-dimethoxy-phenyl)acryloylmorpholine,

and a variety of fungicides such as dodecylguanidine acetate, 3-[3-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]glutarimide, hexachlorobenzene, methyl N-(2,6-dimethylphenyl)-N-(2-furoyl)-DL-alaninate, DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl)-alanine methyl ester, N-(2,6-dimethylphenyl)-N-chloroacetyl-D,L-2-amino-butylolactone, DL-N-(2,6-dimethylphenyl)-N-(phenylacetyl)alanine methyl ester, 5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-2,4-dioxo-1,3-oxazolidine, 3-[3,5-dichlorophenyl(5-methyl-5-methoxymethyl)-1,3-oxazolidine-2,4-dione, 3-(3,5-dichlorophenyl)-1-isopropylcarbamoylethylhydantoin, N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide, 2-cyano-[N-(ethylaminocarbonyl)-2-methoximino]acetamide,

3,5-Dichloro-N-(3-chloro-1-ethyl-1-methyl-2-oxo-propyl)-4-methyl-benzamide, 1-(3-Bromo-6-methoxy-2-methyl-phenyl)-1-(2,3,4-trimethoxy-6-methyl-phenyl)-methanone, 1-[2-(2,4-dichloro-phenyl)pentyl]-1H-1,2,4-triazole, 2,4-difluoro- α -(1H-1,2,4-triazolyl-1-methyl)benzhydryl alcohol, N-(3-chloro-2,6-dinitro-4-trifluoromethylphenyl)-5-trifluoromethyl-3-chloro-2-aminopyridine, 1-((bis(4-fluorophenyl)methylsilyl)methyl)-1H-1,2,4-triazole.

30

Synthesis Examples

With due modification of the starting compounds, the protocols shown in the synthesis examples below were used for obtaining 5 further compounds I. The resulting compounds I, together with physical data, are listed in Table I which follows.

Example 1 Preparation of diethyl (2-fluoro-6-methylphenyl)-malonate

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Diethyl malonate (0.49 mol) was added to a mixture of sodium hydride (0.51 mol) and 1,4-dioxane (140 ml) at 60°C within 2 hours. The mixture was stirred for 10 minutes at 60°C and copper (I) bromide (0.05 mol) was added. After 15 minutes, a solution of 15 2-bromo-3-fluorotoluene (0.25 mol) in 10 ml 1,4-dioxane was added. The reaction mixture was kept at 100°C for about 15 hours and after cooling to about 15°C 35 ml of 12N Hydrochloric acid were added. The precipitate was filtered off, the filtrate was extracted with diethyl ether. The organic phase was separated, 20 dried and filtered. The filtrate was evaporated to yield 42 g of the title compound.

Example 2 Preparation of 5,7-dihydroxy-6-(2-fluoro-6-methylphenyl)-[1,2,4]-triazolo-[1,5- α]pyrimidine

25

A mixture of 3-amino-1,2,4-triazole (14 g), diethyl (2-fluoro-6-methylphenyl)-malonate (0.17 mol, Ex. 1) and tributylamine (50 ml) is heated at 180°C for six hours; after cooling to 70°C a solution of 21g sodium hydroxide in 200 ml water was 30 added and the reaction mixture was stirred for 30 minutes. The organic phase was separated off and the aqueous phase was extracted with diethyl ether. The aqueous phase was acidified with concentrated hydrochloric acid. The precipitate was collected by filtration and dried to yield 41 g of the title compound.

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Example 3 Preparation of 5,7-dichloro-6-(2-fluoro-6-methylphenyl)-[1,2,4]-triazolo-[1,5- α]pyrimidine

A mixture of the compound from Ex. 2 (30 g) and phosphorous oxy- 40 chloride (50 ml) was refluxed for eight hours. Phosphorous oxychloride was partly distilled off. The residue was poured into a mixture of dichloromethane and water. The organic layer was separated, dried and filtered. The filtrate was concentrated in vacuo to yield 27 g of the title compound of mp. 130°C.

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Example 4 Preparation of 5-chloro-6-(2-fluoro-6-methylphenyl)-7-isopropylamino-[1,2,4]-triazolo[1,5- α]pyrimidine [I-8]

5 A mixture of isopropylamine (1.5 mmol), triethylamine (1.5 mmol) and dichloromethane (10 ml) was added to a solution of 1.5 mmol of the product from Ex. 3 in 20 ml dichloromethane under stirring. The reaction mixture was stirred for about 16 hours at about 20 to 25°C and subsequently washed with 5 % hydrochloric
10 acid. The organic layer was separated, dried and filtered. The filtrate was evaporated and the residue was chromatographed to yield 0.46 g of the title compound of mp. 128°C.

Example 5 Preparation of 5-cyano-6-(2-fluoro-6-methylphenyl)-7-(4-methylpiperidin-1-yl)-[1,2,4]-triazolo[1,5- α]pyrimidine [I-49]
15

A mixture of 0.1 mol compound I-9 and tetraethylammonium cyanide (0.25 mol) in 750 ml Dimethylformamide (DMF) was stirred for
20 16 hours at about 20 to 25°C. To this mixture was added water and methyl-tert.butyl ether (MTBE), the organic phase was separated, washed with water, dried and filtered. The filtrate was evaporated and the residue was chromatographed to yield 6.51 g of the title compound of mp. 211°C.

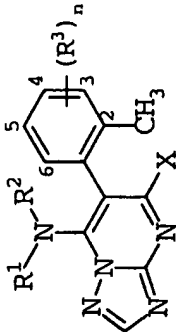
25 Example 6 Preparation of 5-methoxy-6-(2-fluoro-6-methylphenyl)-7-(4-methylpiperidin-1-yl)-[1,2,4]-triazolo[1,5- α]pyrimidine [I-50]

30 After having added a solution of sodium methanolate (30%, 71.5 mmol) to a solution of 65 mmol of compound I-9 in 400 ml dry methanol was added this mixture was stirred for about 16 hours at about 20 to 25°C. Methanol was evaporated and the residue was dissolved with dichloromethane. The organic phase was washed with
35 water, dried and filtered. The filtrate was evaporated and the residue was chromatographed to yield 4.32 g of the title compound of mp. 142°C.

40

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Table I



No.	R ¹	R ²	(R ³) _n	X	phys. data (m.p. [°C]; ¹ H-NMR δ [ppm])
I-1	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4,6-(CH ₃) ₂	Cl	131
I-2	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4,6-(CH ₃) ₂	Cl	138
I-3	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-OCH ₃ -6-CH ₃	Cl	74
I-4	(±) CH(CH ₃)-CH(CH ₃) ₃	H	4-OCH ₃ -6-CH ₃	Cl	163
I-5	CH ₂ CF ₃	H	4-OCH ₃ -6-CH ₃	Cl	191
I-6	H	H	6-F	Cl	250
I-7	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	6-F	Cl	124
I-8	CH(CH ₃) ₂	H	6-F	Cl	128
I-9	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	Cl	142
I-10	cyclopentyl	H	6-F	Cl	159
I-11	CH ₂ CH ₃	CH ₂ CH ₃	6-F	Cl	147
I-12	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	6-F	Cl	124
I-13	CH(CH ₃) ₂	CH ₃	6-F	Cl	159

No.	R ¹	R ²	(R ³) _n	X	phys. data (m.p. [°C]; ¹ H-NMR δ [ppm])
I-14	(±) CH(CH ₃)-CH ₂ CH ₃	H	6-F	Cl	115
I-15	(S) CH(CH ₃)-CH ₂ CH ₃	H	6-F	Cl	123
I-16	(R) CH(CH ₃)-CH ₂ CH ₃	H	6-F	Cl	129
I-17	(±) CH(CH ₃)-CH(CH ₃) ₂	H	6-F	Cl	A) 133 / B) 138
I-18	(S) CH(CH ₃)-CH(CH ₃) ₂	H	6-F	Cl	A) 120 / B) 130
I-19	(R) CH(CH ₃)-CH(CH ₃) ₂	H	6-F	Cl	A) 119 / B) 131
I-20	(±) CH(CH ₃)-CH(CH ₃) ₃	H	6-F	Cl	A) 148 / B) 174
I-21	(S) CH(CH ₃)-CH(CH ₃) ₃	H	6-F	Cl	A) 160 / B) 203
I-22	(R) CH(CH ₃)-CH(CH ₃) ₃	H	6-F	Cl	A) 159 / B) 203
I-23	(±) CH(CH ₃)-CF ₃	H	6-F	Cl	A) 149 / B) 56
I-24	(S) CH(CH ₃)-CF ₃	H	6-F	Cl	A) 166 / B) 70
I-25	(R) CH(CH ₃)-CF ₃	H	6-F	Cl	A) 167 / B) 70
I-26	CH ₂ CF ₃	H	6-F	Cl	173
I-27	H	H	4-F	Cl	281
I-28	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-F	Cl	115
I-29	CH(CH ₃) ₂	H	4-F	Cl	94
I-30	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4-F	Cl	168
I-31	cyclopentyl	H	4-F	Cl	141
I-32	CH ₂ CH ₃	CH ₂ CH ₃	4-F	Cl	156
I-33	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	4-F	Cl	121

No.	R ¹	R ²	(R ³) _n	X	phys. data (m.p. [°C]; ¹ H-NMR δ [ppm])
I-34	CH(CH ₃) ₂	CH ₃	4-F	Cl	153
I-35	(±) CH(CH ₃) - CH ₂ CH ₃	H	4-F	Cl	118
I-36	(S) CH(CH ₃) - CH ₂ CH ₃	H	4-F	Cl	125
I-37	(R) CH(CH ₃) - CH ₂ CH ₃	H	4-F	Cl	126
I-38	(±) CH(CH ₃) - CH(CH ₃) ₂	H	4-F	Cl	132
I-39	(S) CH(CH ₃) - CH(CH ₃) ₂	H	4-F	Cl	124
I-40	(R) CH(CH ₃) - CH(CH ₃) ₂	H	4-F	Cl	124
I-41	(±) CH(CH ₃) - CH(CH ₃) ₃	H	4-F	Cl	162
I-42	(S) CH(CH ₃) - CH(CH ₃) ₃	H	4-F	Cl	156
I-43	(R) CH(CH ₃) - CH(CH ₃) ₃	H	4-F	Cl	156
I-44	(±) CH(CH ₃) - CF ₃	H	4-F	Cl	163
I-45	(S) CH(CH ₃) - CF ₃	H	4-F	Cl	145
I-46	(R) CH(CH ₃) - CF ₃	H	4-F	Cl	145
I-47	CH ₂ CF ₃	H	4-F	Cl	167
I-48	CH ₂ CF ₃	H	4-F-6-CH ₃	Cl	220
I-49	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	CN	211
I-50	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	OCH ₃	142
I-51	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		6-F	CH ₃	145
I-52	cyclopentyl	H	4,6-(CH ₃) ₂	Cl	200
I-53	CH ₂ CH ₃	CH ₂ CH ₃	4,6-(CH ₃) ₂	Cl	105

No.	R ¹	R ²	(R ³) _n	X	phys. data (m.p. [°C]; ¹ H-NMR δ [ppm])
I-54	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	4,6-(CH ₃) ₂	Cl	99
I-55	(±) CH(CH ₃)-CH ₂ CH ₃	H	4,6-(CH ₃) ₂	Cl	191
I-56	(S) CH(CH ₃)-CH ₂ CH ₃	H	4,6-(CH ₃) ₂	Cl	184
I-57	(R) CH(CH ₃)-CH ₂ CH ₃	H	4,6-(CH ₃) ₂	Cl	184
I-58	(±) CH(CH ₃)-CH(CH ₃) ₂	H	4,6-(CH ₃) ₂	Cl	107
I-59	(S) CH(CH ₃)-CH(CH ₃) ₂	H	4,6-(CH ₃) ₂	Cl	87
I-60	(R) CH(CH ₃)-CH(CH ₃) ₂	H	4,6-(CH ₃) ₂	Cl	87
I-61	(±) CH(CH ₃)-CH(CH ₃) ₃	H	4,6-(CH ₃) ₂	Cl	79
I-62	(S) CH(CH ₃)-CH(CH ₃) ₃	H	4,6-(CH ₃) ₂	Cl	81
I-63	(R) CH(CH ₃)-CH(CH ₃) ₃	H	4,6-(CH ₃) ₂	Cl	81
I-64	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-Cl	Cl	137
I-65	CH(CH ₃) ₂	H	4-Cl	Cl	136
I-66	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4-Cl	Cl	173
I-67	cyclopentyl	H	4-Cl	Cl	147
I-68	CH ₂ CH ₃	CH ₂ CH ₃	4-Cl	Cl	167
I-69	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	4-Cl	Cl	149
I-70	CH(CH ₃) ₂	CH ₃	4-Cl	Cl	159
I-71	(±) CH(CH ₃)-CH ₂ CH ₃	H	4-Cl	Cl	128
I-72	(S) CH(CH ₃)-CH ₂ CH ₃	H	4-Cl	Cl	114
I-73	(R) CH(CH ₃)-CH ₂ CH ₃	H	4-Cl	Cl	114

No.	R ¹	R ²	(R ³) _n	X	phys. data (m.p. [°C]; ¹ H-NMR δ [ppm])
I-74	(±) CH(CH ₃) - CH(CH ₃) ₂	H	4-Cl	Cl	116
I-75	(S) CH(CH ₃) - CH(CH ₃) ₂	H	4-Cl	Cl	130
I-76	(R) CH(CH ₃) - CH(CH ₃) ₂	H	4-Cl	Cl	130
I-77	(±) CH(CH ₃) - CH(CH ₃) ₃	H	4-Cl	Cl	159
I-78	(S) CH(CH ₃) - CH(CH ₃) ₃	H	4-Cl	Cl	159
I-79	(R) CH(CH ₃) - CH(CH ₃) ₃	H	4-Cl	Cl	159
I-80	(±) CH(CH ₃) - CF ₃	H	4-Cl	Cl	184
I-81	(S) CH(CH ₃) - CF ₃	H	4-Cl	Cl	143
I-82	(R) CH(CH ₃) - CF ₃	H	4-Cl	Cl	143
I-83	CH ₂ CF ₃	H	4-Cl	Cl	206
I-84	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	4-CH ₃	Cl	158
I-85	CH(CH ₃) ₂	H	4-CH ₃	Cl	145
I-86	CH ₂ CH ₃	CH ₂ CH ₃	4-CH ₃	Cl	141
I-87	(±) CH(CH ₃) - CH ₂ CH ₃	H	4-CH ₃	Cl	122
I-88	(S) CH(CH ₃) - CH(CH ₃) ₃	H	4-CH ₃	Cl	108
I-89	(R) CH(CH ₃) - CH(CH ₃) ₃	H	4-CH ₃	Cl	108
I-90	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		4-COOCH ₃	Cl	8.45(s); 8.05(s); 7.95(d); 7.25(d); 4.0(s); 3.85(d); 3.45(d); 2.7(t); 2.65(t); 2.25(s); 1.55(m); 1.45(m); 1.25(m); 0.9(d)

No.	R ¹	R ²	(R ³) _n	X	phys. data (m.p. [°C]; ¹ H-NMR δ [ppm])
I-91	(R) CH(CH ₃)-CH(CH ₃) ₂	H	4-COOCH ₃	Cl	8.35(s); 8.1(s); 8.0(d); 7.35(d); 6.2(m); 3.95(s); 3.1(m); 2.25(s); 1.55(sept); 1.2(d); 0.95(d); 0.9(d)
I-92	(S) CH(CH ₃)-CF ₃	H	4-COOCH ₃	Cl	8.4(s); 8.15(s); 8.05(d); 7.35(m); 5.7(m); 4.6(m); 3.95(s); 2.3(s); 2.25(s); 1.4(d); 1.3(d)
I-93	CH ₂ CF ₂ CF ₃	H	6-F	Cl	162
I-94	CH ₂ CF ₂ CF ₂ CF ₃	H	6-F	Cl	165
I-95	CH ₂ CF ₂ CF ₃	H	4-F	Cl	176
I-96	CH ₂ CF ₂ CF ₂ CF ₃	H	4-F	Cl	138
I-97	CH ₂ CF ₂ CF ₃	H	4-Cl	Cl	164
I-98	CH ₂ CF ₂ CF ₂ CF ₃	H	4-Cl	Cl	126
I-99	H	H	4-Cl	Cl	276

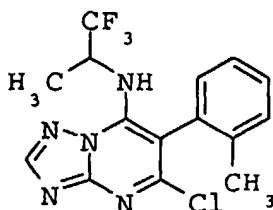
In some cases of chiral groups R¹ and due to the hindered rotation of the phenyl group two diastereomers A) and B) exist which may differ in their physical properties.

Examples of the action against harmful fungi

The fungicidal action of the compounds of the formula I was
5 demonstrated by the following experiments:

The active compounds, separately or together, were formulated as
a 10% emulsion in a mixture of 70% by weight of cyclohexanone,
20% by weight of Nekanil® LN (Lutensol® AP6, wetting agent having
10 emulsifying and dispersant action based on ethoxylated
alkylphenols) and 10% by weight of Wettol® EM (nonionic
emulsifier based on ethoxylated castor oil) and diluted with
water to the desired concentration.

15 Compound A known from WO-A 98/46608 (No. 9) served as comparative
active compound:



20 Comparison trial 1 - Fungicidal control of early blight on toma-
toes (*Alternaria solani*)

Young seedlings of tomato plants of the variety "Große Fleischto-
mate St. Pierre" were grown in pots to the 2 to 4 leaf stage.
These plants were sprayed to run-off with an aqueous suspension,
30 containing the concentration of active ingredient mentioned in
the table below, prepared from a stock solution containing 10 %
of the active ingredient, 85 % cyclohexanone and 5 % emulsifier.
The next day, the treated plants were inoculated with an aqueous
suspension of *Alternaria solani* containing 0.2×10^6 spores per
35 ml. Then the trial plants were immediately transferred to a hu-
mid chamber. After 6 days at 20 to 23°C and a relative humidity
close to 100 %, the extent of fungal attack on the leaves was vi-
sually assessed as % diseased leaf area.

40 In this test, the plants which had been treated with 63 ppm of
compounds I-23 and I-24, resp., showed an infection of not more
than 3%, whereas the the plants treated with 63 ppm of the
comparison compound A were infected to 15%, and the untreated
plants were infected to 90%.

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Comparison trial 2 - Fungicidal control of powdery mildew on wheat caused by *Blumeria graminis* f. sp. *tritici*

The first fully developed leaves of pot grown wheat of the variety "Kanzler" were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below, prepared from a stock solution containing 10 % of the active ingredient, 85 % cyclohexanone and 5 % emulsifier. The next day the treated plants were inoculated with spores of *Blumeria graminis* f. sp. *tritici* by shaking heavily infested stock plants over the treated pots. After cultivation in the greenhouse for 7 days at 22-26°C and a relative humidity between 60 to 90 % the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

15

In this test, the plants which had been treated with 63 ppm of compounds I-23 and I-24, resp., showed an infection of not more than 3%, whereas the the plants treated with 63 ppm of the comparison compound A were infected to 30%, and the untreated plants were infected to 85%.

20

Comparison trial 3 - Fungicidal control of grape downy mildew (*Plasmopara viticola*)

Grape cuttings of the cultivar "Müller-Thurgau" were grown in pots to the 4 to 5 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below, prepared from a stock solution containing 10 % of the active ingredient, 85 % cyclohexanone and 5 % emulsifier. The plants were allowed to air-dry. The next day they were inoculated with an aqueous spore suspension of *Plasmopara viticola* by spraying it at the lower leaf-side. Then the trial plants were immediately transferred for 24 h to a humid chamber with 22 - 24°C and a relative humidity close to 100 %. For a period of 5 days, cultivation followed in a greenhouse at 20 - 25°C and a relative humidity about 50-80 %. To stimulate the outbreak of the disease symptoms, the plants were transferred to a humid chamber again for 24 hours. Then the extent of fungal attack on the lower leaf surface was visually assessed as % diseased leaf area.

In this test, the plants which had been treated with 250 ppm of compounds I-23 and I-24, resp., showed an infection of not more than 7%, whereas the the plants treated with 250 ppm of the comparison compound A, and the untreated plants were infected to 80%.

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Use Example 1 - Fungicidal control of early blight on tomatoes (*Alternaria solani*)

The test was conducted as described in Comparison trial 1.

5

In this test, the plants which have been treated with 250 ppm of compounds I-7, I-9, I-10, I-28, I-30, I-35, I-38, I-41, I-44, I-66, and I-83, resp., showed no infection, whereas the untreated plants were infected to 90%.

10

Use Example 2 - Fungicidal control of powdery mildew on wheat caused by *Blumeria graminis* f. sp. *tritici*

The test was conducted as described in Comparison trial 2.

15

In this test, the plants which have been treated with 250 ppm of compounds I-14, I-28, I-30, I-35, I-38, I-41, and I-44, resp., showed an infection of not more than 5%, whereas the untreated plants were infected to 85%.

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Use Example 3 - Fungicidal control of grape downy mildew (*Plasmopara viticola*)

Leaves of potted vines of the "Müller Thurgau" variety were

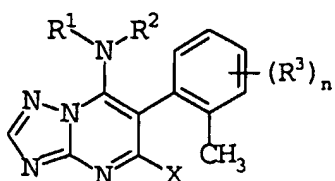
25 sprayed with aqueous liquors made from a stock solution consisting of 10% of active ingredient, 85% of cyclohexanone, and 5% of emulsifier. To assess the duration of action, the plants were set up, after the sprayed-on layer had dried, in the greenhouse for 8 days. Then the leaves were infected with a zoospore suspension of the fungus *Plasmopara viticola*, first placed in a vapour-saturated chamber at 24°C, and then kept for 5 days in a greenhouse at 20 to 30°C. To accelerate and intensify the sporangio-
30 phore discharge, the plants were then again placed in the moist chamber for 16 hours. The extent of fungus attack was then assessed on the undersides of the leaves.
35

In this test, the plants which have been treated with 250 ppm of compounds I-7, I-9, I-10, I-35, I-38, and I-44, resp., showed an infection of 3 to 40%, whereas the untreated plants were infected
40 to 80%.

45

Claims:

1. Substituted 6-(2-tolyl)-triazolopyrimidines of formula I



I

in which

R^1 and R^2 independently denote hydrogen or

C_1 - C_{10} -alkyl, C_2 - C_{10} -alkenyl, C_2 - C_{10} -alkynyl, or C_4 - C_{10} -alkadienyl, C_1 - C_{10} -haloalkyl, C_2 - C_{10} -haloalkenyl, C_3 - C_{10} -cycloalkyl, phenyl, naphthyl, or

C_3 - C_{10} -cycloalkyl, phenyl, naphthyl, or

5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

where R^1 and R^2 radicals may be unsubstituted or partly or fully halogenated or may carry one to three groups R^a ,

R^a is cyano, nitro, hydroxyl, C_1 - C_6 -alkyl, C_1 - C_6 -haloalkyl, C_3 - C_6 -cycloalkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -haloalkoxy, C_1 - C_6 -alkylthio, C_1 - C_6 -alkylamino, di- C_1 - C_6 -alkylamino, C_2 - C_6 -alkenyl, C_2 - C_6 -alkenyloxy, C_2 - C_6 -alkynyl, C_3 - C_6 -alkynyloxy and C_1 - C_4 -alkylenedioxy; or

R^1 and R^2 together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted by one to three R^a radicals;

R^3 is halogen, cyano, C_1 - C_{10} -alkyl, C_1 - C_{10} -alkoxy, C_1 - C_{10} -haloalkyl, or $C(=O)A$, wherein

42

A is hydrogen, hydroxy, C₁-C₈-alkyl, C₁-C₈-alkoxy, amino, C₁-C₈-alkylamino, or di-(C₁-C₈-alkyl)amino;

n is an integer from 1 to 4; and

5

X is halogen, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₈-alkenyloxy.

2. Compounds of formula I according to claim 1, in which

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R¹ is straight chained or branched C₁-C₆-alkyl, C₂-C₆-alkenyl, C₃-C₉-cycloalkyl, or C₁-C₁₀-haloalkyl, and

R² is hydrogen or C₁-C₆-alkyl, or

15

R¹ and R² together with the interjacent nitrogen atom represent a heterocyclic ring with 5 or 6 carbon atoms being optionally substituted with one or two C₁-C₆-alkyl groups.

20

3. Compounds of formula I according to claims 1 or 2 in which R² is hydrogen.

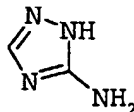
4. Compounds of formula I according to claims 1 to 3 in which X is halogen.

25

5. Compounds of formula I according to claims 1 to 4 in which (R³)_n is 4-(C₁-C₈-alkoxy-carbonyl) or 4-cyano.

6. A process for the preparation of compounds of formula I as defined in claim 4 which comprises reacting 5-amino-1,2,4-triazole

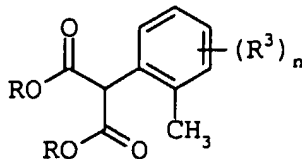
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with 2-phenyl-substituted malonic acid ester of formula II,

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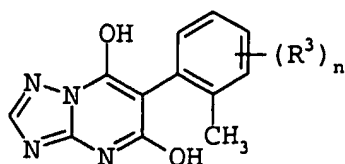


II

wherein R³ and n are as defined in formula I, and R denotes C₁-C₆-alkyl, under alkaline conditions, to yield compounds of formula III,

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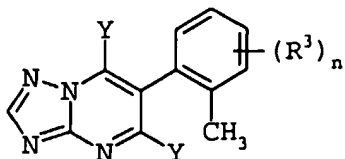
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III

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which are subsequently treated with a halogenating agent to give 5,7-dihalogen-6-phenyl-triazolopyrimidines of formula IV

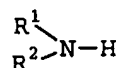


IV

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in which Y is halogen with an amine of formula V

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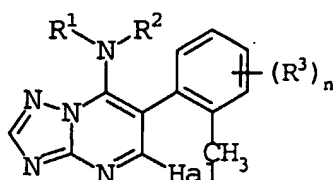
V

in which R¹ and R² are as defined in formula I to produce compounds of formula I.

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7. A process for the preparation of compounds of formula I according to claim 1 wherein X is cyano, C₁-C₁₀-alkoxy, or C₁-C₁₀-haloalkyl, which comprises reacting 5-halogen-triazolopyrimidine of formula I

25



I (X=Hal)

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with compounds of formula VI,



VI

which are, dependent from the value of X' to be introduced, an anorganic cyano salt, an alkoxylate, haloalkoxylate or an alkenyloxylate, resp., wherein M is ammonium-, tetraalkylammonium-, alkalimetal- or earth metal cation, to produce compounds of formula I.

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- 40 8. Intermediates of formulae II, III, and IV as defined in claim 6.

9. A composition suitable for controlling phytopathogenic fungi, comprising a solid or liquid carrier and a compound of the formula I as claimed in claim 1.

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10. A method for controlling phytopathogenic fungi, which comprises treating the fungi or the materials, plants, the soil or the seed to be protected against fungal attack with an effective amount of a compound of the formula I as claimed in
5 claim 1.

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07D487/04 A01N43/90 //(C07D487/04,249:00,239:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 204 269 B1 (W. PFRENGLE ET AL.) 20 March 2001 (2001-03-20) column 3, line 50 -column 3, line 55; claims 1-10; example 7 ---	1-9
P,Y	WO 02 46195 A (BASF AG) 13 June 2002 (2002-06-13) claims 1-10 ---	1-9
Y	US 5 948 783 A (K.-J. PEES ET AL.) 7 September 1999 (1999-09-07) claims 1-8 ---	1-9
Y	FR 2 795 073 A (AMERICAN CYANAMID CO.) 22 December 2000 (2000-12-22) claims 1-5 ---	1-9
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

29 October 2002

Date of mailing of the international search report

07/11/2002

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 02 38565 A (BASF AG) 16 May 2002 (2002-05-16) claims 1-9; table A ----	1-9
P,Y	WO 02 50077 A (BAYER AG) 27 June 2002 (2002-06-27) claims 1-9 ----	1-9
X	EP 0 071 792 A (BASF AG) 16 February 1983 (1983-02-16) page 10, line 23; claims 1-8 ----	1-9
Y	WO 98 46608 A (AMERICAN CYANAMID CO.) 22 October 1998 (1998-10-22) cited in the application claims 1-10 ----	1-9
Y	EP 0 550 113 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 7 July 1993 (1993-07-07) claims 1-10 -----	1-9

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6204269	B1	20-03-2001	US 5986135 A	16-11-1999
			BR 9904354 A	12-09-2000
			CN 1250052 A	12-04-2000
			EP 0989130 A1	29-03-2000
			JP 2000119275 A	25-04-2000
			ZA 9905673 A	30-03-2000
WO 0246195	A	13-06-2002	WO 0246195 A1	13-06-2002
			AU 2362901 A	18-06-2002
US 5948783	A	07-09-1999	NONE	
FR 2795073	A	22-12-2000	FR 2795073 A1	22-12-2000
WO 0238565	A	16-05-2002	AU 2183102 A	21-05-2002
			WO 0238565 A2	16-05-2002
WO 0250077	A	27-06-2002	DE 10063115 A1	27-06-2002
			AU 3167602 A	01-07-2002
			WO 0250077 A2	27-06-2002
EP 71792	A	16-02-1983	DE 3130633 A1	17-02-1983
			AT 11539 T	15-02-1985
			AU 553663 B2	24-07-1986
			AU 8665982 A	10-02-1983
			CA 1180329 A1	01-01-1985
			CS 226748 B2	16-04-1984
			DD 202093 A5	31-08-1983
			DE 3262143 D1	14-03-1985
			DK 341682 A ,B,	02-02-1983
			EP 0071792 A2	16-02-1983
			GR 76193 A1	03-08-1984
			HU 188325 B	28-04-1986
			IE 53269 B1	28-09-1988
			JP 1634879 C	20-01-1992
			JP 2061955 B	21-12-1990
			JP 58043974 A	14-03-1983
			US 4567263 A	28-01-1986
			ZA 8205498 A	27-07-1983
WO 9846608	A	22-10-1998	AU 735730 B2	12-07-2001
			AU 6867198 A	11-11-1998
			BG 103805 A	30-06-2000
			BR 9808531 A	23-05-2000
			CN 1257502 T	21-06-2000
			EE 9900486 A	15-06-2000
			EP 0975635 A1	02-02-2000
			HU 0001993 A2	28-10-2000
			JP 2001520650 T	30-10-2001
			NO 994973 A	13-10-1999
			NZ 500143 A	29-06-2001
			PL 336164 A1	05-06-2000
			SK 141499 A3	11-09-2001
			TR 9902552 T2	22-05-2000
			TW 460476 B	21-10-2001
			WO 9846608 A1	22-10-1998
			ZA 9803054 A	11-10-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 550113	A	07-07-1993	EP 0550113 A2	07-07-1993
			EP 0782997 A2	09-07-1997
			GR 3033916 T3	30-11-2000
			AT 159256 T	15-11-1997
			AT 192154 T	15-05-2000
			AU 667204 B2	14-03-1996
			AU 3043592 A	01-07-1993
			BR 9205172 A	06-07-1993
			CA 2086404 A1	01-07-1993
			CN 1075144 A ,B	11-08-1993
			CN 1141119 A ,B	29-01-1997
			DE 69222746 D1	20-11-1997
			DE 69222746 T2	12-02-1998
			DE 69230977 D1	31-05-2000
			DE 69230977 T2	09-11-2000
			DK 550113 T3	09-02-1998
			DK 782997 T3	07-08-2000
			ES 2108727 T3	01-01-1998
			ES 2147411 T3	01-09-2000
			GR 3025920 T3	30-04-1998
			HK 1010105 A1	23-06-2000
			HU 217349 B	28-01-2000
			IL 104244 A	13-07-1997
			JP 5271234 A	19-10-1993
			NZ 245581 A	26-07-1995
			PL 297160 A1	06-09-1993
			PL 171579 B1	30-05-1997
			PT 782997 T	29-09-2000
			RU 2089552 C1	10-09-1997
			SG 47563 A1	17-04-1998
			US 5593996 A	14-01-1997
			ZA 9210043 A	28-07-1993